Development of Glass-Glass Fusion Bonding Recipes for All-Glass Nanofluidic Devices

Undergraduate Honors Thesis

Presented in Partial Fulfillment of the Requirements for Graduation with Distinction in the Department of Mechanical Engineering at

The Ohio State University

By

Wenhao Deng

The Ohio State University

April 2015

Examination Committee:

Professor Shaurya Prakash, Advisor

Professor Carlos Castro

Abstract

Glass is a desired material for microfluidic and nanofluidic chips due to chemical inertness, temperature stability, and optical clarity. Given the desire to maintain chemical uniformity for flow conduits, it is well known that thermal fusion bonding is the preferred method to bond two distinct glass substrates. Furthermore, thermal fusion bonding is known to achieve higher bond strength compared to other bonding techniques (e.g., anodic bonding). The purpose of this research is to develop a reliable recipe for successful fusion bonding of all-glass nanochannels. In this research, a device with inverted Y-shaped nanochannels is used as a model system. The nanochannels are 500 nm in depth and are fabricated via standard lithography and wet etching. The width of the channel is 100 μm at the entry of the channel and reduces to 50 μm at each bifurcated leg. The channel is etched in a sodium borosilicate glass slide which is subsequently capped with soda-lime-silica glass slide in which holes were drilled to act as reservoirs for working fluid inlet to subsequently seal the channel from the ambient environment. In this research, we have investigated thermal bonding parameters including the variation of temperature, the use of weights to apply a constant pressure on the glass slides, and the use of surface activation processes. Our results indicate that sealed glass-glass channels can be bonded at a temperature of 600℃ over 10 hours along with simultaneous application of weight over the bonding area (a load of 1.14 kg corresponds to a pressure of 9.3 kPa applied over the entire area of the channel containing cover glass). The devices will be used for subsequent electrical manipulation of ions and molecules.

Dedication

To my parents and teachers, who set me on the path that led me to where I'm at today.

Acknowledgements

I would first of all like to thank my advisor, Prof. Shaurya Prakash. My accomplishments over these past semesters are a result of his constant support, guidance, and encouragement. He has pushed me to work harder than I ever thought I could, and as a result I have done more than I ever imagined I could. He was always willing to sit down with me and discuss the project or hold lengthy conversations over email. He always give me encouragement when I faced challenges and difficulties. There aren't enough pages for me to express how thankful I am for his unwavering faith in my abilities.

The project would not have existed without my graduate mentor Kaushik Rangharajan. I really appreciated all the page-long like emails explaining difficult concepts that seems so much more confusing in books and journal articles. It was always encouraging to me, as an undergraduate student, to see his enthusiasm about this study knowing that he had so many other interesting and important projects going on.

I owe a huge thank you to Dr. Emily Rosenthal for being so generous in giving so much help in every of my presentations and writing drafts. She also give me encouragement when I facing challenges. It is no exaggeration when I say that the completion of my project wouldn't have been possible without her.

A big thank you also goes to my fellow MSNS lab mates, who have provided a lot of suggestions, constructive criticism, and encouragement. And finally, I have to thank my friends and family for being so understanding, especially during the last quarter of the project. Their love and support makes all of the sweat and tears worth it. One of the greatest rewards of this work is the opportunity to make them proud.

Vita

123 West Lane Avenue, Columbus, Ohio, 43210/Tel:614-477-8040/Email:deng.248@osu.edu

Field of Study

The Ohio State University-Columbus May 2015

Bachelor of Science in Mechanical Engineering

- GPA: 3.779/4.0 (Dean's List/ Engineering Honors Program)
- Honors Thesis: Development of Glass-Glass Fusion Bonding Recipes for All-Glass Nanofluidic Devices

Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

1.1 Lab-on-a-chip and fluid manipulation application

Micro- and nano-fabricated fluidic analytical systems have attracted much interest from researchers in chemical, medical, and biological fields [1] because better process control and a faster response of the system, faster analysis and response times due to short diffusion distances and lower fabrication costs.

The introduction of chemical processes on-chip in the mid-1990s led to development of lab-on-a-chip (LoC) or micro-total analysis systems (μ-TAS) with the aim of performing one or several laboratory scale techniques for separations and detections on a single chip. For instance, micro- and nanopumps can be used to imitate the behavior of the heart to move a mass of fluid and salt from water is filtered with membranes to mimic kidney operation. As we can see from the examples above, the goal is to use miniaturized systems that can manipulate fluids to perform a variety of unit operations on a single chip, which making the single chip a multi-function unit cell. This multi-function unit cell consume lower fluid volumes, less waste and lower reagents costs. It also has a faster analysis and response speed and better process control due to the faster response of the system compared to traditional systems [1].

For example, our group has shown selective flow control in 100 μm wide and 20 μm deep channels made in glass chips to direct flow by functionalizing surfaces with a fluorinated molecule to render channels hydrophobic. Figure 1 shows an optical microscope image of the flow in channels as a consequence of part of the device with a Y-shaped channel geometry showing flow control [1].

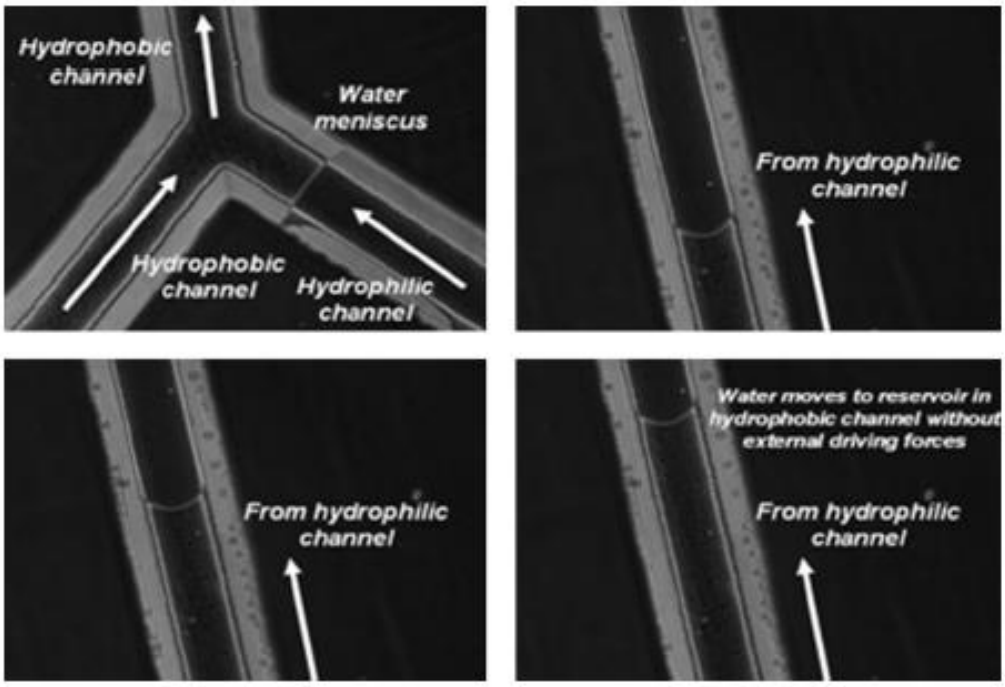


Figure 1. Selective transport of DI water in a channel network functionalized with a fluorinated molecule, FDTS or heptadecafluoro-1, 1, 2, 2, hydrodecal trichlorosilane. [1]

Microfluidics generally refers to the study of fluidic systems with critical operational lengths in the 1–100 μm range, while nanofluidics is defined as the study of fluidic systems with critical operational length at 1–100 nm. Figure 2 shows another example of a microfluidic-based biosensor that can be incorporated onto a wristwatch. The lab-on-a-chip system relies on manipulation of small volumes of fluid in microchannels using microvalves and the flow of fluids in the channels is driven by electric-field.

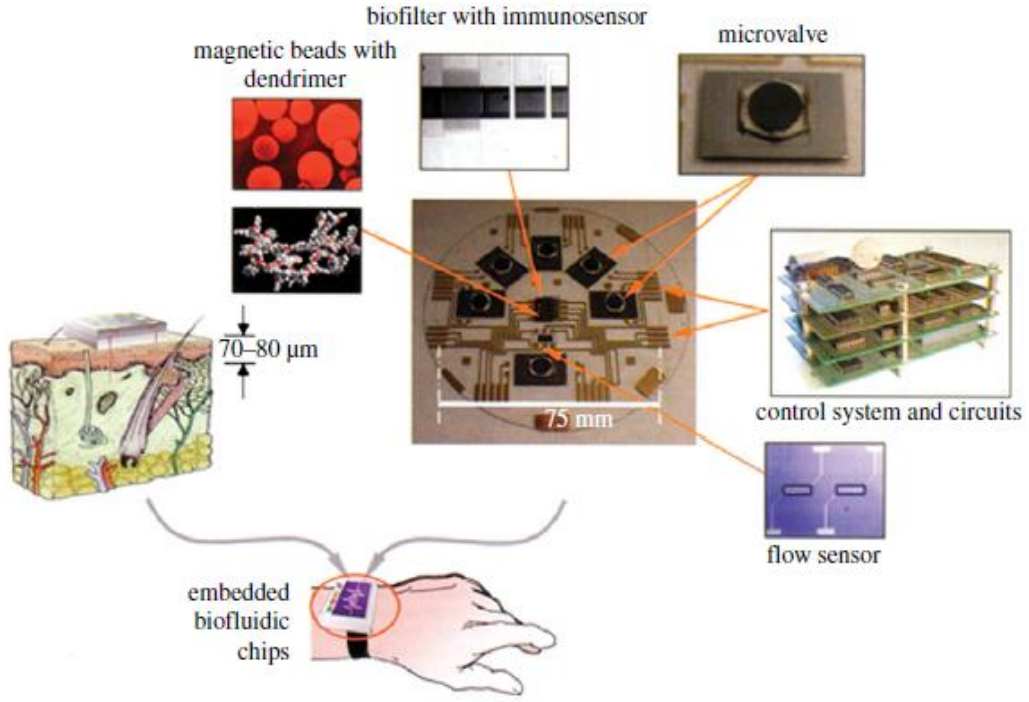


Figure 2. Microfluidic-based biosensor that can be incorporated onto a wristwatch. [2]

Glass has been the dominant substrate materials in many lab-on-a-chip applications due to the fact that the fabrication methods were well developed by the semiconductor and MEMS industries [3] and the glass substrates are dimensionally stable, optically transparent allowing for the optical methods to image and chemical inert allowing for different activation steps. Glass micro and nanofluidic devices offer the advantages of chemical resistance, surface properties, optical properties, and thermal stability.

Micro- and nanofluidic architectures in glass substrates have been made by several micromachining methods, such as wet or dry etching, injection molding, and power blasting [4]. Once micro- or nanodevice features have been fabricated on a substrate, the features must be isolated from the outside environment to protect the sample from contamination or interferences toward sensing. Therefore, the devices are often sealed using a cover layer using well-established

bonding methods. For example, Pinti *et al*. reported the use of a polydimethylsiloxane (PDMS) sandwich layer [5]. The main goal of this honors project was to add a glass 'roof' to previously fabricated glass micro- and nanochannels (3 other glass walls in a trench configuration). Figure 3 is the schematic description of nanochannel fabrication process on glass substrate.

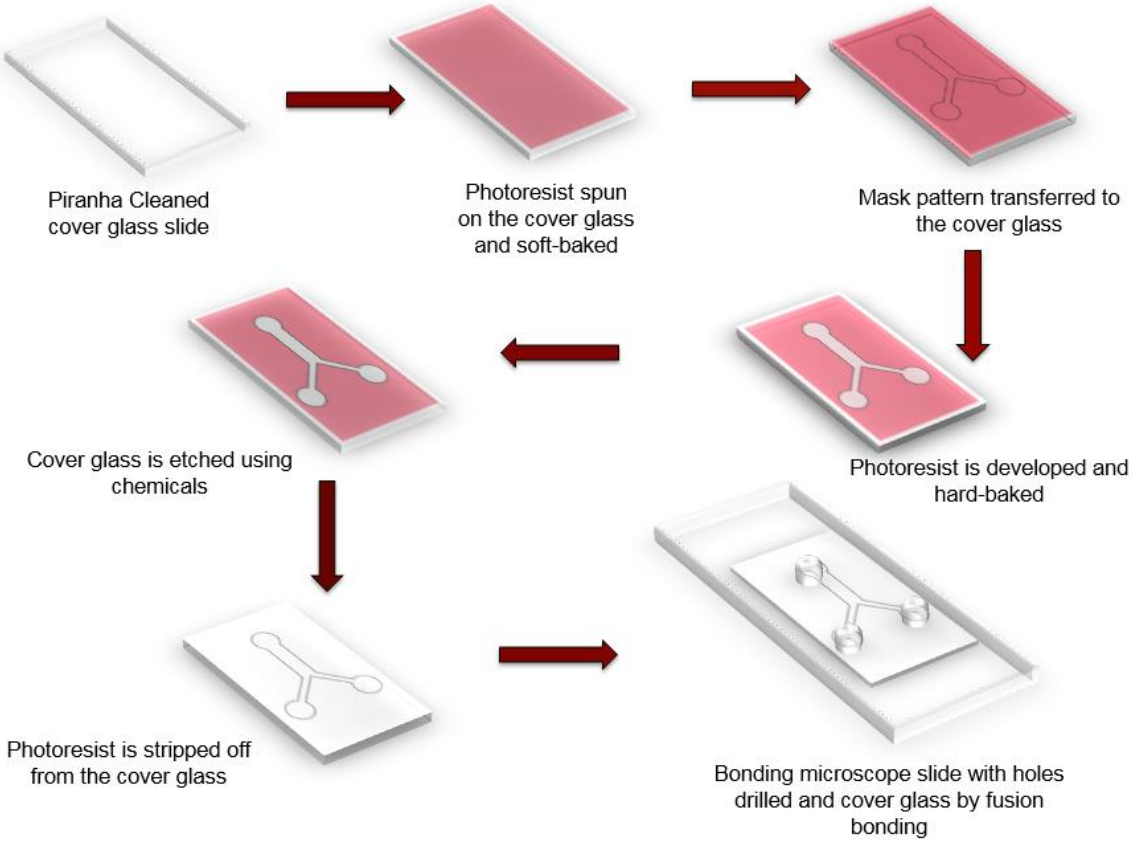


Figure 3. Schematic description of nanochannel fabrication process on glass substrate.

Achieving successful roof bonding is critically important for operation and use of these all-glass microfluidic and nanofluidic devices. If there is not good bonding, the channel will leak or allow the entry of contaminants. A number of glass-glass bonding methods have been reported, ranging from thermal bonding, low-temperature bonding, HF bonding, anodic bonding and

bonding with glue or an adhesive as an intermediate layer [6]. Some more recently reported glass-to-glass bonding processed include bonding with thin films as intermediate layer in which the temperature does not exceed 400°C [7], and low energy metal glass bonding. The recent review on the various glass bonding techniques is available by Niklaus et al. [8].

Our focus is developing fusion bonding methods because they ensure an all-glass, fully enclosed micro/nanochannel. Different methods for fusion bonding of glass devices have been investigated and the bonding process must satisfy several requirements to preserve the desired channels. The very first requirement is that the bond should preserve the colorlessness and transparency of the glass structures. No particles or contamination may form between the bond and cause glass structures to become opaque. Another very important requirement is that the seal between glass slides should be sufficient enough to prevent leakage while still preserving the desired depth of the nano- and microfluidic channels.

1.2 Glass Fusion Bonding

Fusion bonding (also called direct bonding) refers to a bonding process without any additional intermediate materials. Fusion bonding is typically used for glass-to-glass or silicon-to-silicon bonding [1]. The basic fusion bonding process entails pressing two glass substrates together and applying heat for a long duration. In glass fusion bonding, glass substrates may be heated up to 600℃ which allows the material to soften and fuse with the opposite substrate, but without melting. The chemical reaction behind glass to glass bonding is:

$$\text{Si-OH} + \text{Si-OH} \rightarrow \text{Si-O-Si} + H_2O.$$

The substrates need to be sufficiently clean, flat, and smooth, and the bonding quality is highly susceptible to particle defects [1]. Some glass to glass bonding methods at low temperature in

which high bond strengths can be achieved in a relatively short time without having to use a furnace with complex temperature regulation have been reported recently[9]. Mao *et al.* (2005) concluded that the low temperature bonding requires a rigorous cleaning procedure prior to bonding and the bond strength could not be as strong as high temperature and the usage of adhesives or glue may block the channels [10]. Although fusion bonding process takes a relatively long processing time, gives a relative low yield rate, and requires high surface flatness, it is still the preferred technique to generate four chemically similar walls compared to other bonding techniques. Mao's group have fully characterized glass-glass fusion bonding techniques for the fabrication of planar nanofluidic channels as thin as 20 nm with aspect ratio (1:250, depth to width) in the glass–glass nanochannels consisting of 2 cm long parallel lines spaced by 5 μm[10]. The goal of this honors research is to develop an all-glass fusion bonding recipe for an inverted Y channel as thin as 500 nm with aspect ratio 1:2000 at the entry of the channel and 1:1000 for each leg. The channel length is 1cm for both the entry part and each leg.

In traditional glass-to-glass fusion bonding, glass is heated to a temperature near to the glass transition temperature (~550℃) and put under pressure to create a seal. The temperature, applied pressure and aspect ratio of the channels are the three main factors that determine the survival of the channels. If the bonding temperature is too high, the channels would be deformed or collapsed due to reflow of glass. If the temperature is too low, bonding will not occur at all [10].

Figure 4 shows failure or collapse of the nanochannel fabrication (cross-sectional view) and the material run into the channel as you can see.

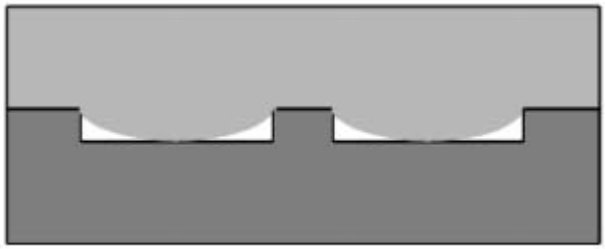


Figure 4. Failure or collapse of the nanochannel fabrication (cross-sectional view). [10]

Based on the established thermal bonding techniques, the purpose of this honors thesis is to develop a an efficient, reliable thermal fusion bonding recipe for the glass-glass structured devices at 500 nm in depth, which will not damage patterned nanochannels in micro-nanochannel devices. This research project is the first project about fusion bonding techniques in our lab and the established recipe can be used for the lab to achieve good glass-glass bonding.

1.3 Materials in micro- and nanofabrication

Glass is an amorphous solid material with main component silica (SiO_2), but varieties of glasses are produced with the inclusion of other compounds to help possess different thermal, mechanical, optical, and chemical properties. The most common type of glass is soda-lime glass (sometimes called window glass) which contains: silica 72% + sodium oxide (Na_2O) 14.2% + lime (CaO) 10.0% + magnesia (MgO) 2.5% + alumina (Al_2O_3) 0.6%. Soda-lime glass is transparent and easily formed. Most of the laboratories and technical glassware are made of borosilicate glass (tradenmame Pyrex), which contains: silica 81% + boric oxide (B_2O_3) 12% + soda (Na_2O) 4.5% + alumina (Al_2O_3) 2.0%. Borosilicate glass has main constituents-silica and boron oxide, which makes them more dimensionally stable in general.

The glass slides used in this project are soda-lime glass and borosilicate glass. Using the same type of glass would be better for fusion bonding because the material would have the same linear

thermal coefficient of expansion, which can reduce the possibility of glass crack during fusion cycle. The reason that we use two different types of glass is because Fisher Scientific does not sell the same types of glass. Also, the glass slides cannot withstand the process of drilling if we use the same slides for the nanochannels because the thickness of the borosilicate glass is only 0.5 mm.

The main related properties for soda-lime glass and borosilicate glass used in this project are summarized in Table 1. The reasons that two different types of glass were used in this project were: 1) The same type of glass are not available commercially (Fisher Scientific) and 2) Glass slides cannot withstand the process of drilling if we use the same slides as the channels (borosilicate glass). As you can see from Table 1 (materials properties from Fisher Scientific), the value of the linear thermal coefficient of expansion for soda lime glass and borosilicate glass is close enough, so it is okay that to use them for fusion bonding cycle.

Table 1: Main related properties for soda-lime glass and borosilicate glass.

Materials	Soda Lime Glass	Borosilicate Glass
Transformation Temperature(℃)	545	557
Linear Thermal Expansion Coefficient ($10^{-6}K^{-1}$)	9.1	7.2
Dimensions (mm) (w × l ×h)	25×75×1	24×50×0.5

1.4 Motivation and objectives

The motivation of the research project is to develop a fusion bonding recipe which can be used to generate an enclosed channel with four chemically similar walls. The reason we need a four

chemically similar walls for micro- and nanochannel is that all the walls will have the same properties in surface charge and surface charge of nanoparticles on membrane potential plays an important role on the lab-on-a-chip device. Ions and molecules will react to all the walls the same way in a chemically similar channel. The devices we made will be used for subsequent electrical manipulation of ions and molecules.

The goal of this research is to establish a fully developed recipe for glass fusion bonding suitable for glass substrates patterned micro/nanochannels. Several key questions about glass-glass fusion bonding has been be investigated, including identifying ideal bonding temperature for the dwelling process (which is the set point temperature in the furnaces), finding ideal applied pressure during the fusion bonding cycle and identifying ideal surface activation steps for glass slides.

The major objectives of this work are:

- Analyze the existing glass-glass bonding techniques.
- Explore the pivotal experimental parameters (temperature profile, applied pressure and surface activation steps) behind the glass-glass bonding process to identify key factors pivotal to bonding.
- Develop an efficient, reliable fusion bonding recipe for the glass-glass structured devices (at 500 nm in depth).

1.5 Overview of thesis

This thesis has 4 chapters. Chapter 2 discusses experimental methods of the whole project. This consists of an experimental overview, as well as the detailed experimental procedures. An introduction to our device design and experiment equipment is also presented in the experimental

overview part and detailed experimental procedures will be given in the experimental procedures part.

Chapter 3 discusses the results of this research and includes two major parts which are the effects of set point temperature and applied pressure and effects of different activation steps. Chapter 4 discusses future work and conclusions of this honors research. Included in this chapter are possible future directions of study, and the key contributions of this thesis.

Chapter 2: Experimental methods

2.1 Experimental Overview

A critical parameter to the process is the transformation temperature (Tg) of the soda lime glass and the borosilicate glass, which is 500-600°C. The glass transformation temperature (Tg) is the reversible transition temperature from a hard and relatively brittle state into a molten or rubber-like state. In order to avoid deformation and collapse of the glass microscope slide and the channel, the operating temperature cannot exceed the transition temperature of the soda lime glass. On the other hand, bonding will not occur if the temperature is too slow, because the condensation will not occur for too low temperature.

Three major procedures to be used in this research project: a) cleaning the glass slides prior to bonding b) glass surface activation steps (optional) and c) identification of the optimal temperature and time conditions for bonding glass-to-glass. It is essential to note that lack of ultra-clean surfaces and/or significant substrate roughness has previously been identified as causes of glass-to-glass bonding failure. Furthermore, for nanochannels, warping the device or partial melting of the glass will likely lead to blocked channels and failed devices.

Before the cleaning procedure, holes were drilled in the microscope slide in alignment with the channel configuration. Subsequently, the microscope slide with the holes and the cover glass with the channel was cleaned using a piranha solution for 20 minutes. The Piranha solution is a mixture of 4:1 concentrated sulfuric acid to 30% hydrogen peroxide solution. The reason we choose Piranha solution is that it can make glass hydrophilic by increasing the number of hydroxyl groups at the surface. Figure 5 shows the cross section of device fabrication.

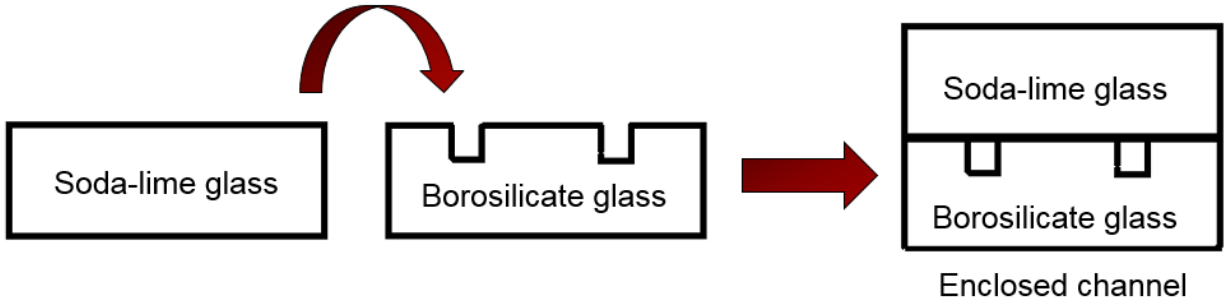


Figure 5. Cross section of device fabrication.

Designed experiments include investigating the bonding parameters and dead-weights necessary for applying a constant pressure on glass slides. The major experimental parameters that must be optimized include: the ramp up rate, the set point, the dwell time and the ramp down rate of temperature. Figures 6 and 7 show the actual assembled device and the 3D view of the device in this research. Figure 8 shows the optical observation of the 250 nm channel sample obtained in the lab. The sample collected from experimentation will be analyzed and tested. Although the glass-glass bonding at high temperature can be achieved successfully with high bonding strengths, the channels may distort and even collapse since the glass material will be softened at high temperature [11]. So, the testing includes whether the nanochannel leaks, whether the nanochannel has collapsed and determining the specific surface properties of the nanochannel.

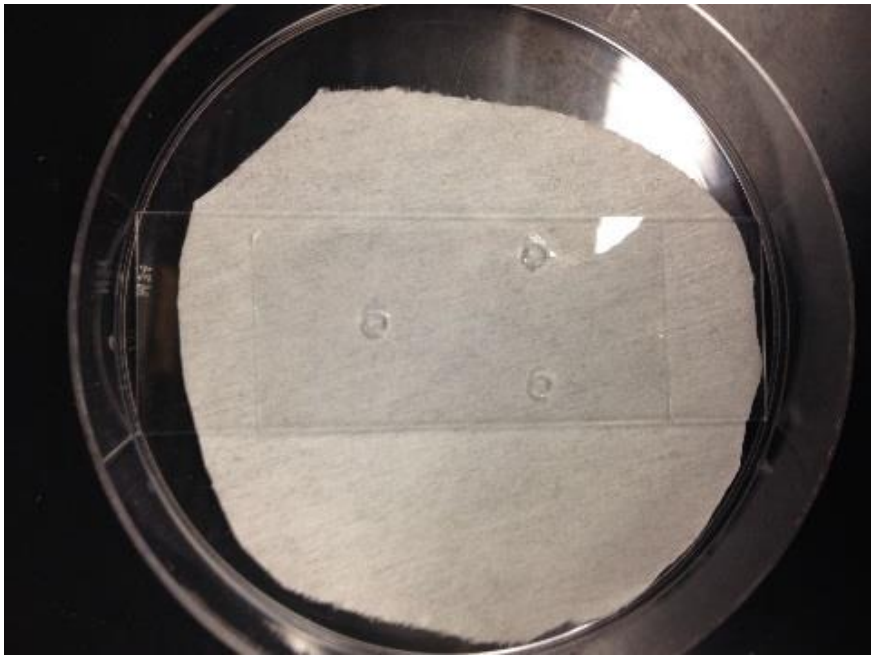


Figure 6. Assembled nanodevice at depth of 500 nm.

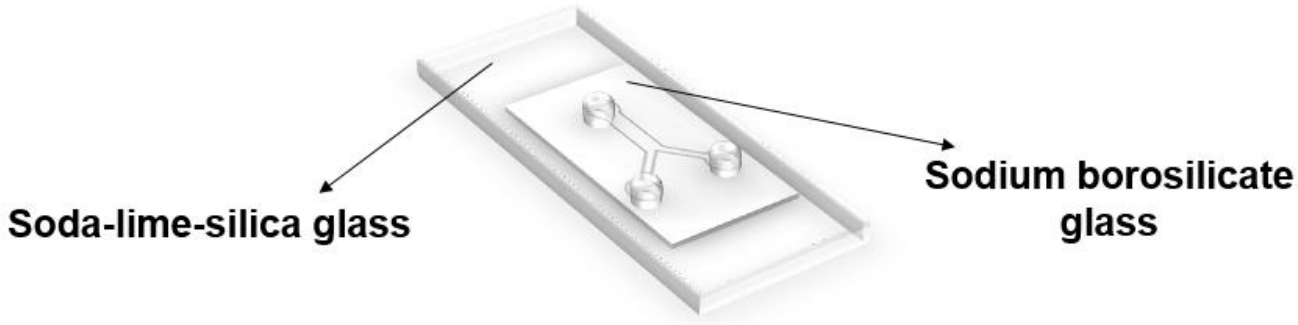


Figure 7. 3D view of the device.

Figure 8. Optical observation of the 250 nm channel.

2.2 Experimental procedures

2.2.1. Materials

Hydrogen peroxide and sulfuric acid were used as received to make piranha solution for glass cleaning. Propanol and acetone were also used as received for glass cleaning. For more details about glass cleaning, please see Appendix A. The DI water was made by Direct-Q® 3 Ultrapure Water Systems in our lab. Calcium hydroxide and ammonium hydroxide were used in the activation steps. Microscope cover glass and plain microscope slides were the glass slides used in this research. All the above materials are purchase from Fisher Scientific.

2.2.2. Instrumentation

Holes in the soda-lime glass were drilled used a 10 inches bench step pulley drill press. The sonicator used in the cleaning steps was a Branson B-3510 ultrasonic cleaners. The high temperature furnaces was controlled by a 2404 temperature controller / programmer made by Schneider Electric (See Appendix C for the operation of the 2404 temperature controller /

programmer). The microscope image was obtained by a Nikon ECLIPSE Ti-U. The constant temperature in the activation steps was achieved by a Fisher Scientific isotemp heated hotplate.

2.2.3. General fabrication procedures

In this project, the general experimental procedures include:

1. Glass slides pre-processing. (Drilling, cleaning and glass surface activation steps)
2. Slides assembly.
3. Programming set point and fusion bonding cycles.
4. Sample analysis. (Leakage test; Bond stress and Optical properties)

2.2.4. Typical experiment

The glass slides cleaning process has two main steps. First, piranha solution is used, which is a mixture of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) with a volume ration of 4:1. .It is used to remove organic residues from glass slides and hydroxylate the glass surfaces (adding OH groups). Please see appendix A for detailed procedures for glass cleaning with piranha solution and appendix B for materials used for glass cleaning with piranha solution.

Once clean and dry, the slides were assembled. The glass slides were sandwiched between two ceramic plates and then weights were applied on the top of the ceramic plates. Different applied pressures were achieved by choosing the different combinations of weights. There were 3 ceramic plates which weigh 0.12 kg, 0.14 kg and 2.27 kg in the lab. These weights can be used for stacking to achieve different applied pressure. The weights were chose by trial and error. Weights in excess of 3 kg lead to cracked samples upon thermal bonding and as a result lighter weights were ordered. Figure 9 is the actual ceramic plates used for applied different pressure in this project. Two devices were fabricated for each experiment, so the contacting area is $2\times24\times50$ (mm^2) when computing the applied pressure.

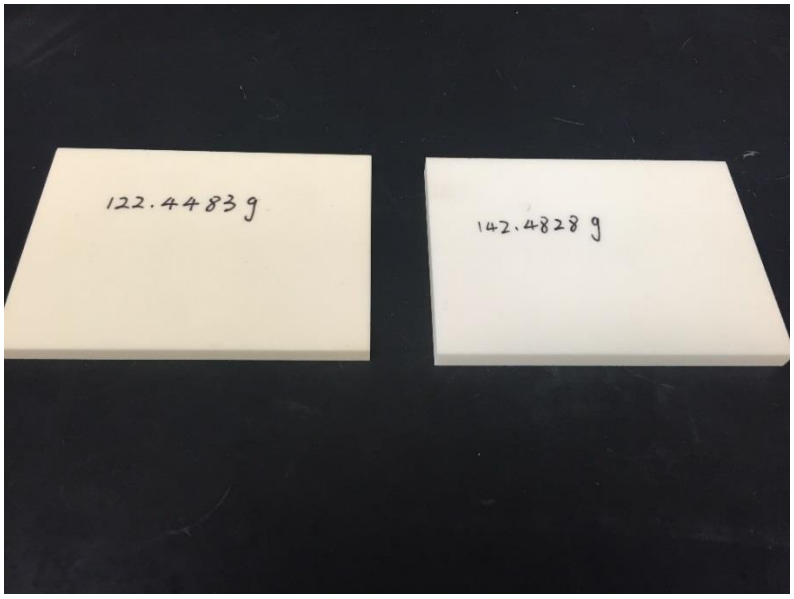


Figure 9. Actual ceramic plates used for applying pressure to glass devices.

After the slides assembly steps, the whole sandwich was put into the digital controlled furnace. Fusion bonding cycle started right after the program has been set point. Figure 10 is an example of heating profile used in fusion bonding and the ramp rate equals to cool down rate, which is 1°C/min.

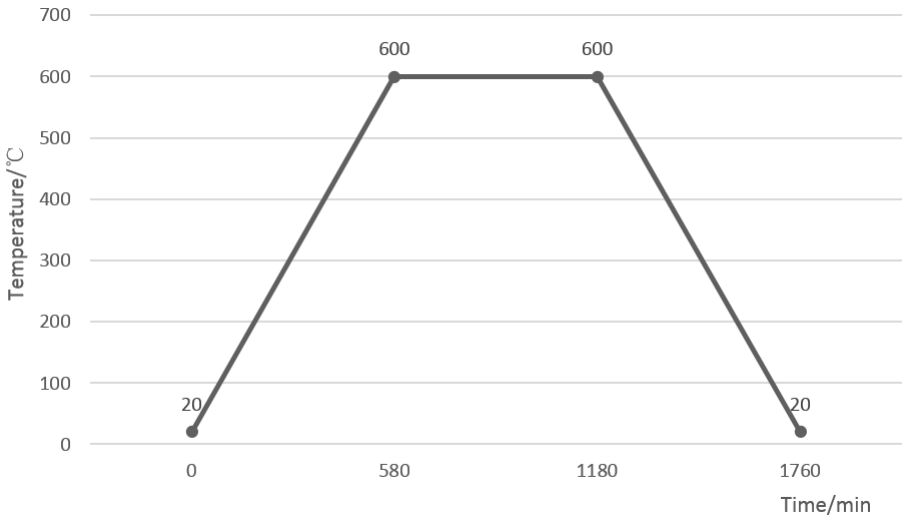


Figure 10. Example of heating profile used in fusion bonding.

Table 2 and 3 are the lists of heating cycle parameters which have been conducted in this project. The ramp rate equals to cool down rate, which is 1°C/min for every experiment. Also, the time for set point temperature is 600 mins for every experiment. In Table 2 and 3, T stands for set point temperature in °C, P stands for applied pressure in kPa and # stands for number of devices under this condition. Different number of devices were decided by trial and error and the set point temperature were chose based on materials properties and literature review.

Table 2. List of heating cycle parameters used in the typical experiment heating cycle.

	T(°C)	P(kPa)	#(number of devices)
1	550	0	4
2	550	9.3	4
3	555	0	4
4	555	9.3	4
5	560	0	6
6	560	9.3	8
7	565	0	6
8	565	9.3	8
9	570	0	10
10	570	0.65	10
11	570	9.3	10
12	570	10.3	10
13	575	0	10
14	575	0.65	10

15	575	9.3	12
16	575	10.3	8

Table 3. List of heating cycle parameters used in the typical experiment heating cycle.

	T(℃)	P(kPa)	#(number of devices)
1	580	0	4
2	580	0.65	6
3	580	9.3	6
4	580	10.3	6
5	585	0	4
6	585	0.65	6
7	585	9.3	6
8	585	10.3	6
9	590	0	4
10	590	0.65	6
11	590	9.3	6
12	590	10.3	6
13	595	0	4
14	595	0.65	6
15	595	9.3	6
16	595	10.3	6
17	600	0	6
18	600	0.65	10

19	600	9.3	12
20	600	10.3	10

The sample analysis was conducted right after the fusion bonding cycles. The analysis included leakage test, bond stress test and optical properties test. For the leakage test, the DI water was drop in the reservoir from which DI water would go through the channel and how the bonding works would be observed under microscope. There were not any quantitative methods for bond stress test. But the devices were tried to separate by tweezers to see whether the bond is strong enough. The optical properties of the channel were observed to see whether the channel has good optical clarity i.e., not observing a visible interference pattern commonly referred to as Newton rings [12]. Figure 11 depicts an example of newton rings in glass structure [12].

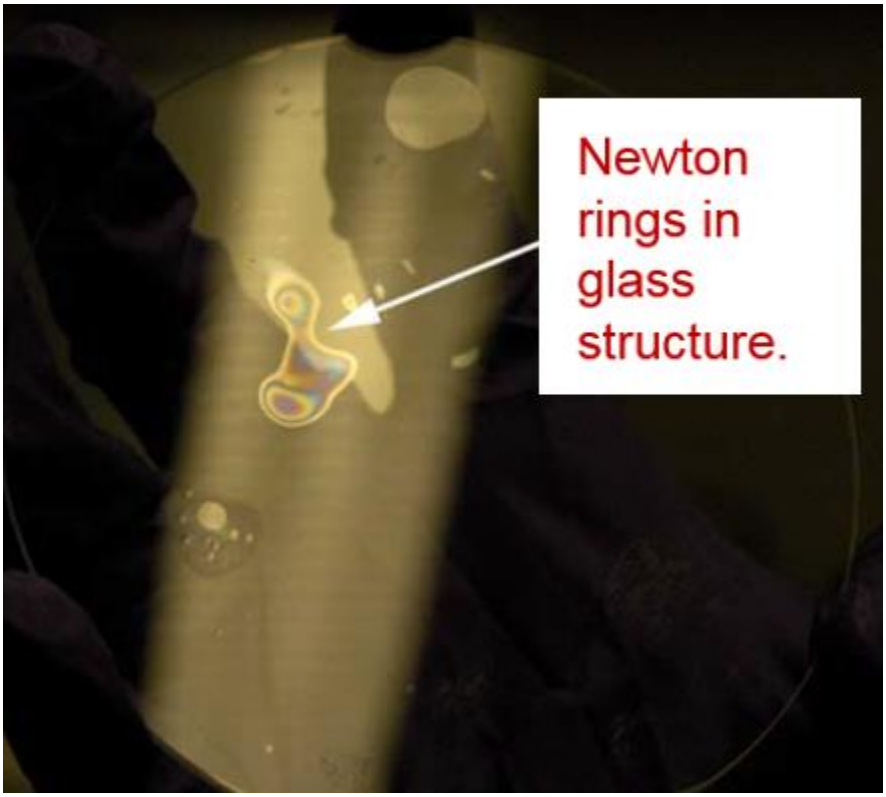


Figure 11. Example of newton rings in glass structure.

2.2.5. Surface activation with ammonium hydroxide and calcium hydroxide

Different chemical surface activation methods were investigated to help achieve better bonding. These experiments were performed in a similar fashion as that of our typical experiment, except for an additional surface activation step that was added right after the Piranha cleaning procedure. Two kinds of surface activation procedures were conducted in this project.

Ammonium hydroxide activation: After 20 mins of piranha cleaning, the device was put into 28% ammonium hydroxide at 50 ℃ for 30 mins. After 30 mins, the glass slides were rinsed using DI water and dried with air. The devices were assembled and then the heating cycles were started. Table 4 presents the list of heating cycle parameters conducted. The ramp-up rate equals to cool down rate, which is 1 ℃/min for every experiment. Also, the time for set point temperature is 600 mins for every experiment. In Table 4, T stands for set point temperature in ℃, P stands for applied pressure in kPa and # stands for number of devices under this condition.

Table 4. List of heating cycle used in the experiment with ammonium hydroxide activation.

	T(℃)	P(kPa)	#(number of devices)
1	550	0	2
2	550	0.65	4
3	550	9.3	4
4	575	0	2
5	575	0.65	4
6	575	9.3	4
7	600	0	2
8	600	0.65	4
9	600	9.3	4

Calcium hydroxide activation: After 20 mins of piranha cleaning, the devices were put into 10mM calcium hydroxide solution for 30 mins. After 30 mins, the glass slides were rinsed using DI water and dried with air. The devices were assembled and the heating cycles were started right after that (as the typical experiment). Table 5 presents the list of heating cycle parameters that has been performed. The ramp-up rate equals to cool down rate, which is 1°C /min for every experiment. Also, the time for set point temperature is 600 mins for every experiment. In Table 5, T stands for set point temperature in °C, P stands for applied pressure in kPa and # stands for number of devices under this condition.

Table 5. List of heating cycle used in the experiment with calcium hydroxide activation.

	T(℃)	P(kPa)	#(number of devices)
1	575	0	2
2	575	0.65	4
3	575	9.3	4
4	600	0	2
5	600	0.65	4
6	600	9.3	4

Chapter 3: Results and discussion

3.1 Results of typical experiment and effects of set point temperature and applied pressure

Set point temperature of 550°C, 555°C, 560°C, 565°C, 570°C, 575 °C, 580°C, 585°C, 590°C, 595°C and 600 °C have been tested with different applied pressure. Other experimental conditions were kept constant, i.e. ramp-up rate equals to cool down rate, which is 1 °C /min and the device was maintained at a given set point temperature for 600 mins (10 hrs.). The same cleaning procedure using piranha solution and the same assembly procedure were applied during each experiment.

Figure 12 is a microscope view that shows poor bonding, a consequence of low set point temperature or not applied weight. Figure 13-21 shows the observation results of devices obtained under different experimental parameters imaged using a microscope.

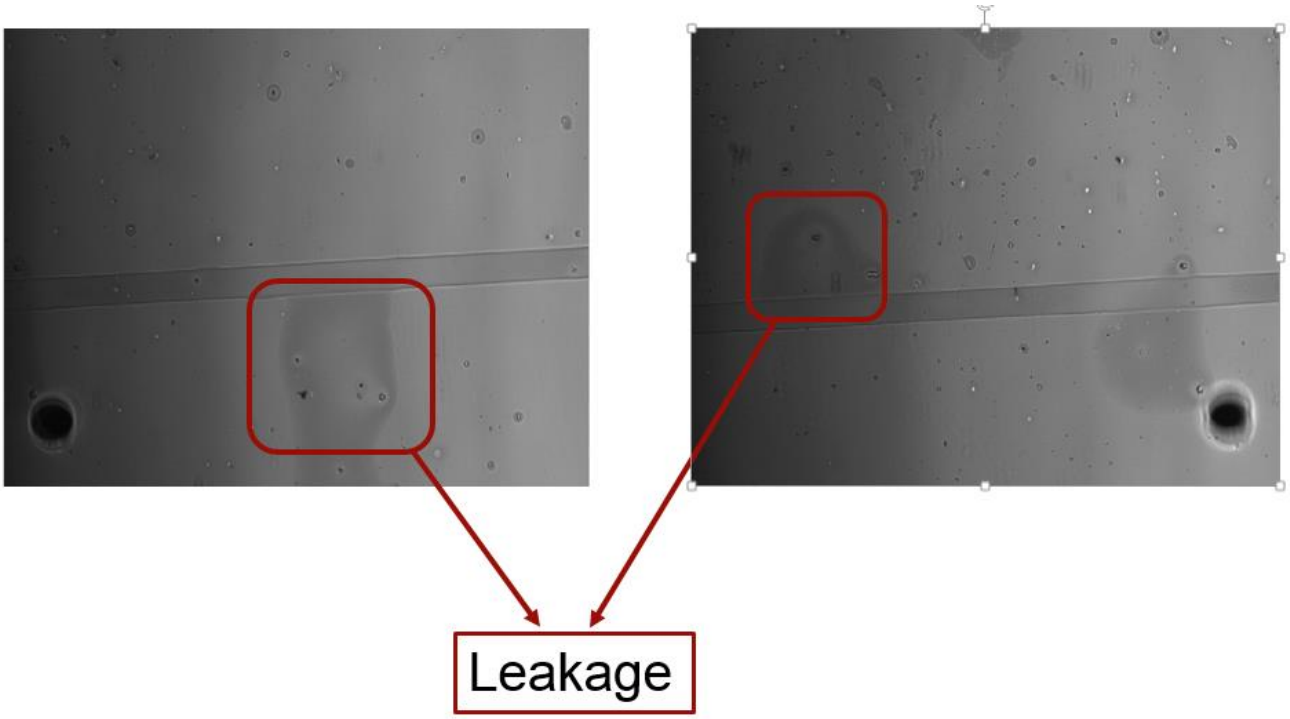


Figure 12: Microscope view of failure of bonding.

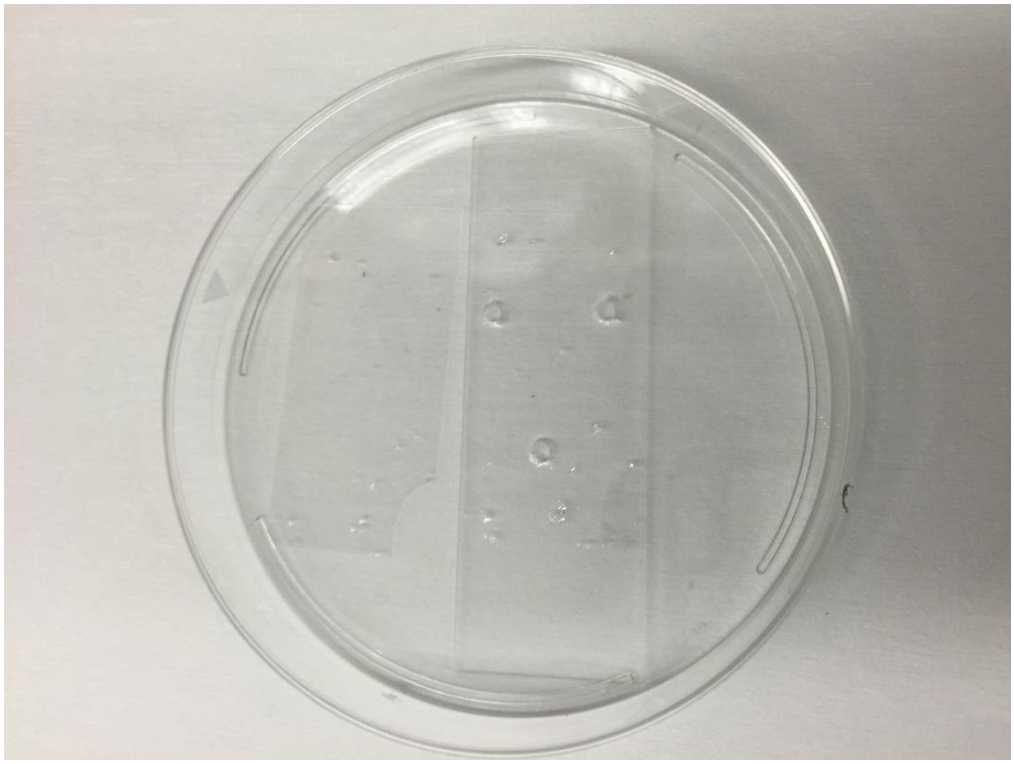


Figure 13. No bonding device due to low set point temperature or low applied temperature.

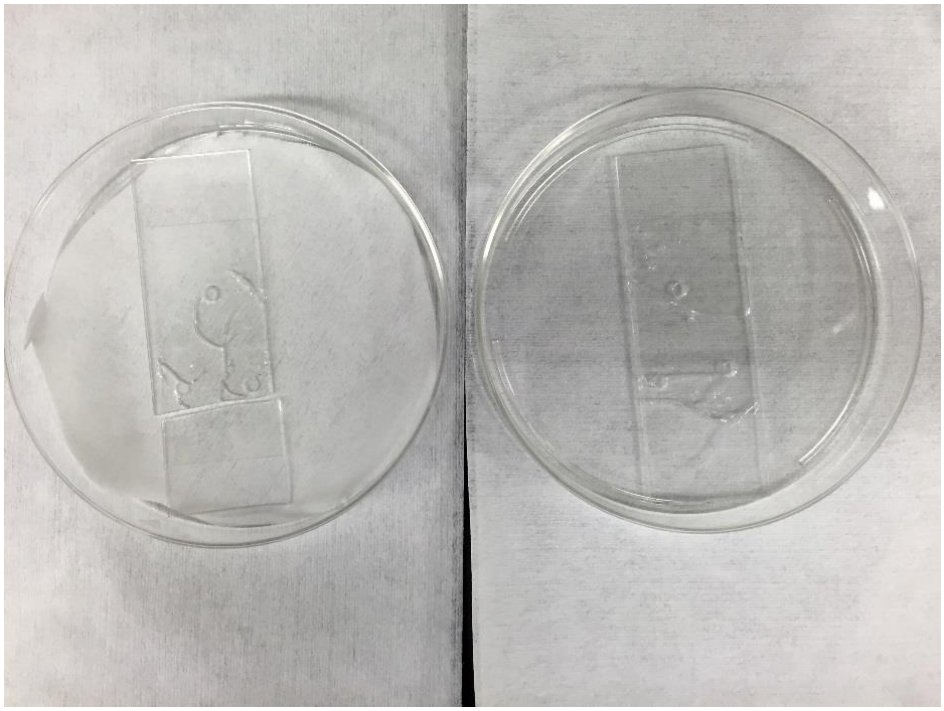


Figure 14. Cracking device at 575 ˚C.

Figure 15. Cracking device at 580 ˚C.

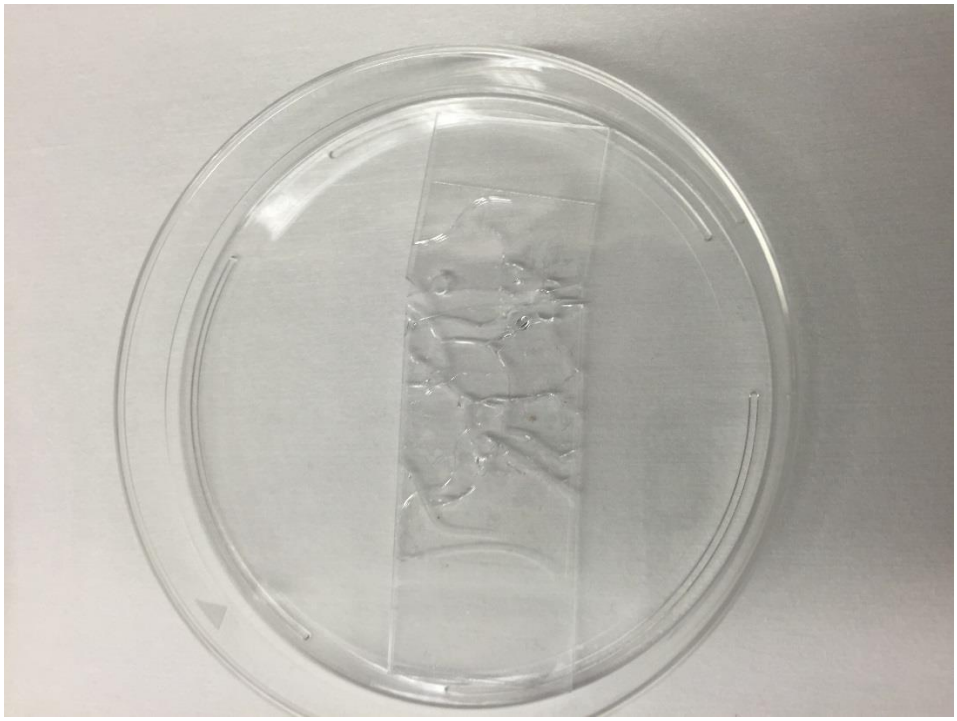


Figure 16. Cracking device at 590°C.

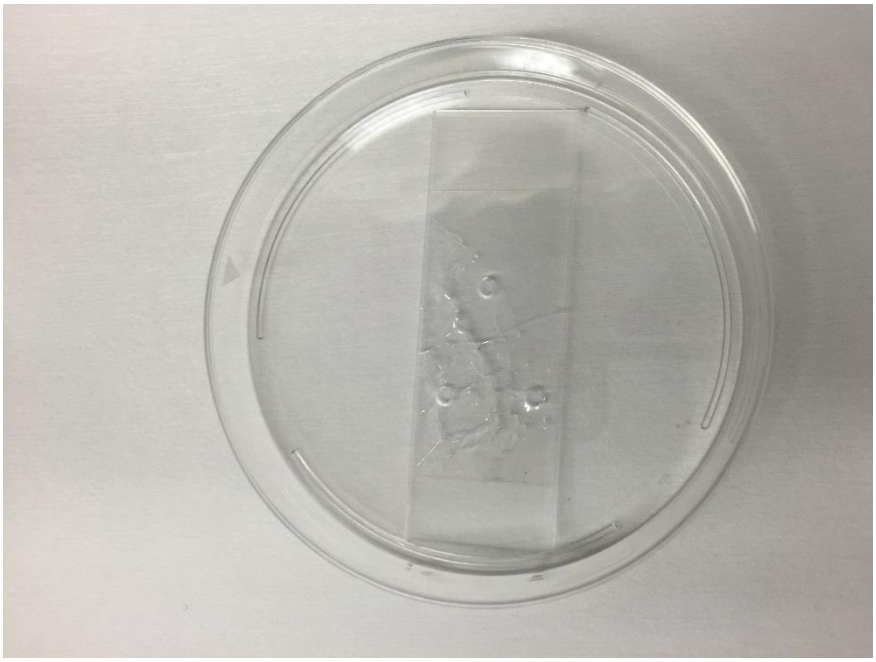


Figure 17. Cracking device at 600°C.

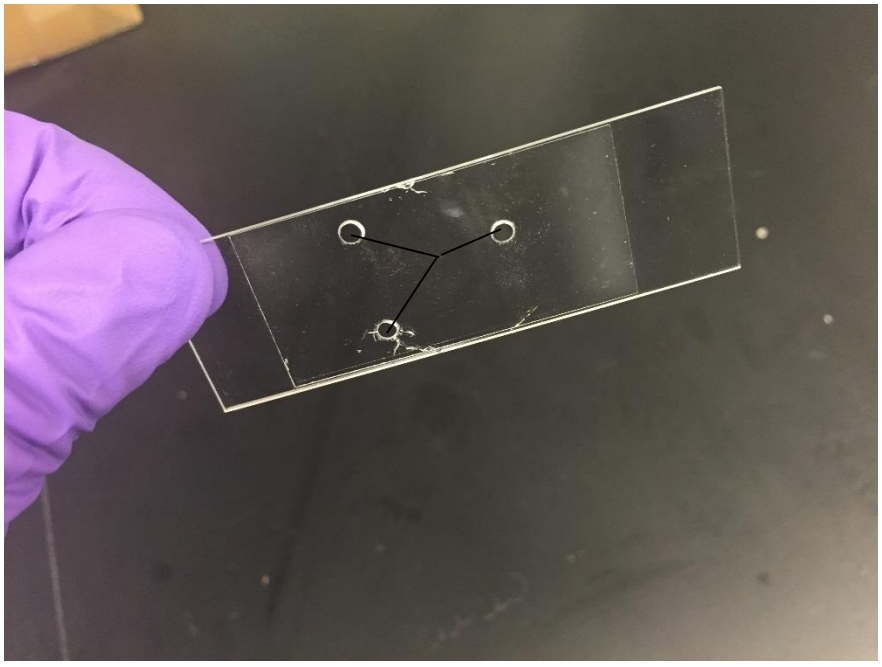


Figure 18.Successful device at 575°C.

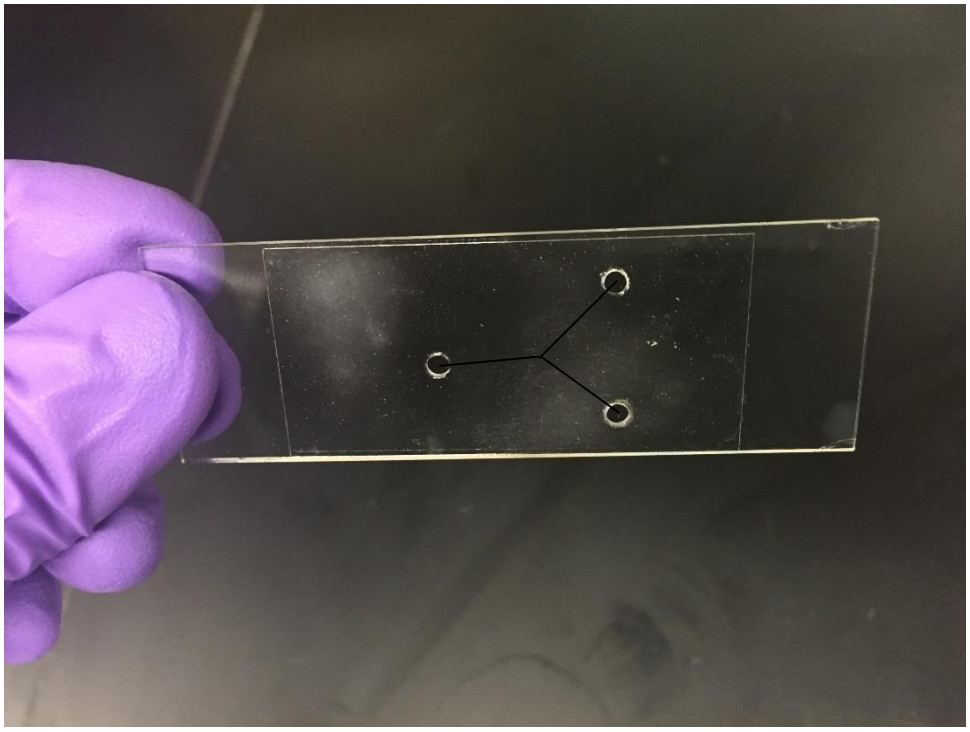


Figure 19.Successful device at 600°C.

Figure 20. Solid bond with few impurities trapped between the surfaces of the glass slides

(600°C)

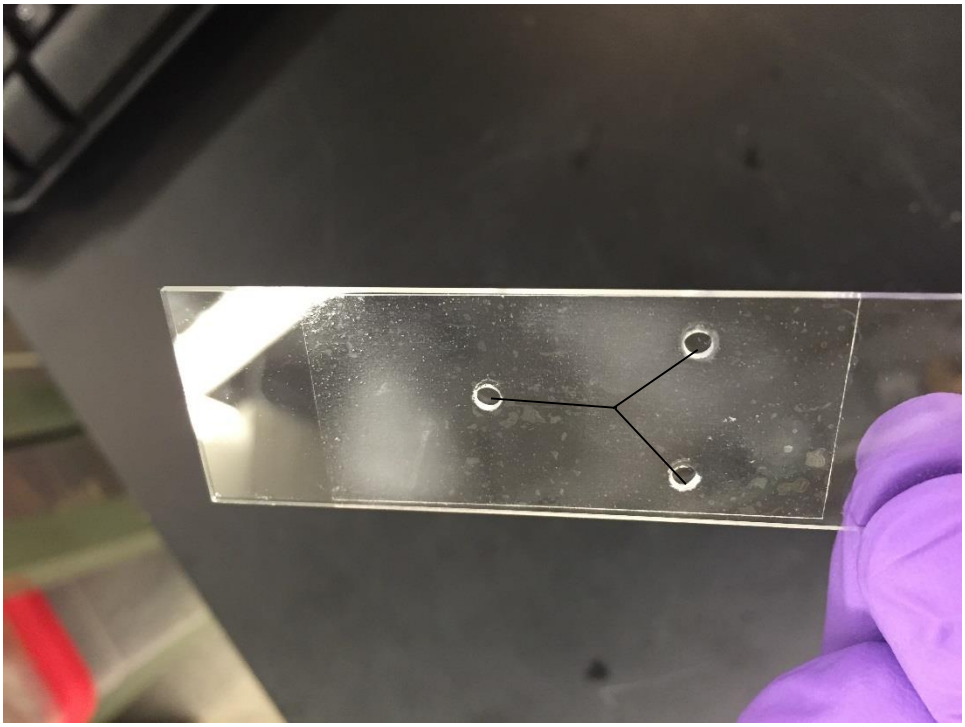


Figure 21. Closer view of solid bond with few impurities trapped between the surfaces of the glass slides (600°C).

Table 6 lists the cumulative results of experiments performed by varying the set point temperature. In table 6, T stands for set point temperature in °C, P stands for applied pressure in kPa and # stands for number of devices we have under this condition.

Table 6. List of results for the typical experiment.

	T(°C)	P(kPa)	#(number of devices)	Observations
1	550	0	4	No bonding
2	550	9.3	4	No bonding
3	555	0	4	No bonding
4	555	9.3	4	No bonding

5	560	0	6	No bonding
6	560	9.3	8	No bonding
7	565	0	6	No bonding
8	565	9.3	8	No bonding
9	570	0	10	No bonding
10	570	0.65	10	No bonding
11	570	9.3	10	4 No bonding +6 Leaking
12	570	10.3	10	4 No bonding + 8Leaking
13	575	0	10	No bonding
14	575	0.65	10	No bonding
15	575	9.3	12	2 Successful + 8 Leaking + 2 Cracking
16	575	10.3	8	2 Successful + 4 Leaking + 4 Cracking
17	580	0	4	No bonding
18	580	0.65	6	No bonding
19	580	9.3	6	4 Leaking + 6 Cracking
20	580	10.3	6	4 Leaking + 6 Cracking
21	585	0	4	No bonding
22	585	0.65	6	No bonding
23	585	9.3	6	2 Leaking + 4 Cracking
24	585	10.3	6	2 Leaking + 4 Cracking
25	590	0	4	No bonding
26	590	0.65	6	No bonding
27	590	9.3	6	2 Leaking + 4 Cracking

28	590	10.3	6	2 Leaking + 4 Cracking
29	595	0	4	No bonding
30	595	0.65	6	No bonding
31	595	9.3	6	4 Leaking + 2 Cracking
32	595	10.3	6	4 Leaking + 2 Cracking
33	600	0	6	No bonding
34	600	0.65	10	No bonding
35	600	9.3	12	4 Successful + 6 Leaking + 2 Cracking
36	600	10.3	10	2 Successful + 6 Leaking + 2 Cracking

We found that poor bonding is observed at lower set point temperatures. We also see that fusion bonding cannot be achieved below 575°C in our cases. We also found that poor bonding is observed when weight is not applied and cracking of glass is seen when the load is increased.

Our results indicate that sealed glass-glass channels can be bonded at a temperature of 600℃ over 10 hours along with simultaneous application of weight over the bonding area (a load of 1.14 kg corresponds to a pressure of 9.3 kPa applied over the entire area of the channel containing cover glass).

3.2 Impact of surface activation on fusion bonding

Ammonium hydroxide and calcium hydroxide activation steps were performed after piranha cleaning. The reason to conduct different surface activation steps is to achieve a more reliable and crack-free bond compared to typical methods. Table 7 and 8 represents the cumulative list of results for ammonium hydroxide and calcium hydroxide activation steps. In table 7 and 8,

T stands for set point temperature in °C, P stands for applied pressure in kPa and # stands for number of devices under this condition. Figure 22 shows a cracking device at 600° C with ammonium hydroxide assisted step.

Table 7. List of results for the ammonium hydroxide assisted experiment.

	T(°C)	P(kPa)	#(number of devices)	Observations
1	550	0	4	No bonding
2	550	0.65	4	No bonding
3	550	9.3	4	No bonding
4	575	0	4	No bonding
5	575	0.65	4	No bonding
6	575	9.3	4	2 Cracking + 2 Leaking
7	600	0	4	No bonding
8	600	0.65	4	No bonding
9	600	9.3	4	Cracking

Table 8. List of results for the calcium hydroxide assisted experiment.

	T(°C)	P(kPa)	#(number of devices)	Observations
1	575	0	4	No bonding
2	575	0.65	4	No bonding
3	575	9.3	4	2 Leaking +2 Cracking
4	600	0	4	No bonding
5	600	0.65	4	No bonding

6	600	9.3	4	2 Successful + 2 Leaking

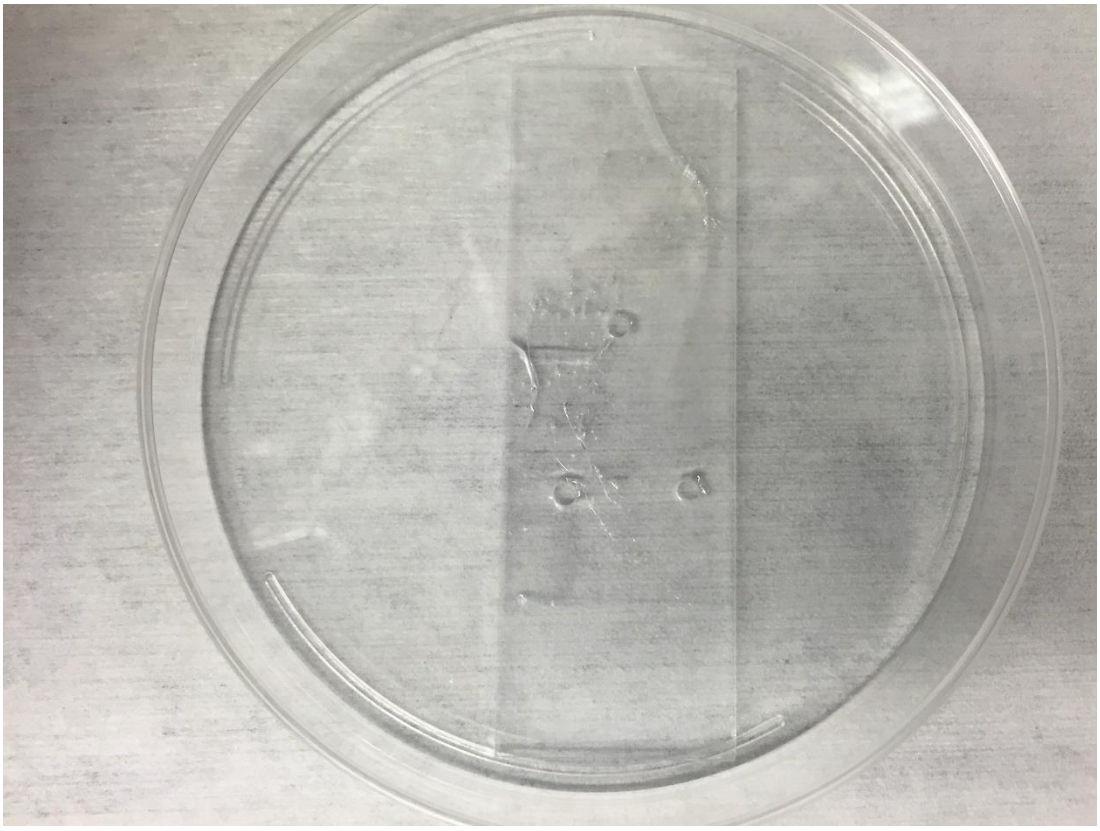


Figure 22. Cracking device at 600°C with ammonium hydroxide assisted step.

Our initial results showed that the use of ammonium hydroxide does not help improve bonding in our cases but the use of calcium ion works in our cases.

For ammonium hydroxide activation, we believed that strong acid cleaning procedures left the silanol groups uncharged, avoiding electrostatic repulsion but the alkaline cleaning solutions leave deprotonated silanol groups that are charged, which produced highly inconsistent results and makes the bonding harder than the typical experiment [13]. For calcium ion activation, we believed that the use of Ca^{2+} allowed us to produce a seal between two glass slides [13].

Chapter 4: Future work and conclusions

4.1 Future Work

The overall future goal of this line of research is to develop an efficient, reliable fusion bonding recipe for the glass-glass structured devices. Later we plan to apply the fusion bonding method to devices with Au electrodes (at or less than 500 nm in depth). Suggestion for next steps in this project are to continue investigating different chemicals activation step to achieve a 100% non-leaking channel. Also, a next step could be to perform a study of quantifying the bond stress achieved by the fusion bonding. The bonding strength should be large enough for most manufacturing and fabrication needs of integrated circuits and transducers. Moreover, the design of the devices could be studied and improved, which means glass-glass structured devices with embedded metal electrodes and patterned nanochannels should be studied to achieve a better bonding. It would also require to reduce the set point temperature to avoid undesirable changes or decomposition of the devices.

4.2 Conclusions

The glass-glass bonding has been realized with the fusion bonding technique at the set point temperature of 600°C over 10 hours along with simultaneous application of weight over the bonding area. The ramp-up rate equals to the cool down rate with is 1°C /min. Poor bonding is observed at lower set point temperature and when weight is not applied. Cracking of glass is seen when the load is increased. Our initial results showed that the use of calcium ion allowed us to produce a seal between two glass slides easily than the typical experiment (without the assistance of any activation steps).

References

1. Prakash, S., Yeom, J., Nanofluidics and Microfluidics: Systems and Applications, Elsevier, 2014.
2. Prakash, S., Pinti, M., Bhushan, B. Theory, Fabrication and Applications of Microfluidic and Nanofluidic Biosensors. Philosophical Transactions of the Royal Society A, 2012, 370(1967), 2269-2303.
3. Becker H, Locascio LE. Review: Polymer microfluidic devices. Talanta 2002; 56:267-87.
4. Schultz, A., et al. "Nano-channel formation using a low-temperature glass-to-glass bonding process." *Proceedings of the Institution of Mechanical Engineers, Part N: Journal of Nanoengineering and Nanosystems* 224.4 (2010): 183-187.
5. Pinti, M., Kambham, T., Wang, B., Prakash, S., Fabrication of Centimeter Long, Ultra-Low Aspect Ratio Nanochannel Networks in Borosilicate Glass Substrates. Journal of Nanotechnology in Engineering and Medicine, 2013, 4(2), 021003.
6. Akiyama, Yoshitake, et al. "Rapid bonding of Pyrex glass microchips." *Electrophoresis* 28.6 (2007): 994-1001.
7. Berthold, A., et al. "Glass-to-glass anodic bonding with standard IC technology thin films as intermediate layers." *Sensors and Actuators A: Physical* 82.1 (2000): 224-228.
8. Niklaus F, Stemme G, Lu J-Q, Gutmann RJ. Adhesive wafer bonding. J Appl Phys 2006; 99:031101.
9. Iles, Alexander, Akio Oki, and Nicole Pamme. "Bonding of soda-lime glass microchips at low temperature." *Microfluidics and Nanofluidics* 3.1 (2007): 119-122.

10. Mao, Pan, and Jongyoon Han. "Fabrication and characterization of 20 nm planar nanofluidic channels by glass–glass and glass–silicon bonding." *Lab on a Chip* 5.8 (2005): 837-844.
11. DeNee, P. B. "Low Energy Metal-Glass Bonding." *Journal of Applied Physics* 40.13 (1969): 5396-5397.
12. Jaime B. Werkmeister & Alexander H. Slocum. "Investigating Different Methods of Bonding Glass Substrates."
13. Peter B. Allen and Daniel T. Chiu. "Calcium-Assisted Glass-to-Glass Bonding for Fabrication of Glass Microfluidic Devices. "*Anal. Chem. 2008, 80, 7153–7157.*

Appendix A

Process Sheet for Glass Cleaning with Piranha Solution

1. Clean tweezers with acetone/IPA/DI/IPA.
2. Clean ceramic staining rack with IPA.
3. Place staining rack in “IPA” beaker and cover with 200 ml of IPA.
4. For each glass slide clean both sides with acetone/IPA/DI/IPA.
5. Load clean glass slide into staining rack that is submerged in the IPA. Be sure the glass slide is fully covered by the IPA.
6. Place “IPA” beaker with slides into the sonicator. Sonicate 5 minutes.
7. Meanwhile prepare the Piranha solution:
    a. Full personal protective gear should be worn when working with Piranha.
    b. Put on gown and face shield. Test gloves with air before putting them on.
    c. Measure out 160ml of 96% Sulfuric acid. Pour into “Piranha” beaker.
    d. Measure out 40ml of 30% Hydrogen Peroxide.
    e. Set the timer for 20 minutes.
8. Remove “IPA” beaker from sonicator and place in the stainless steel tray.
9. Remove staining rack from the “IPA” beaker of IPA. Place in stainless steel tray. Thoroughly dry staining rack and glass slides with air in the stainless steel tray.
10. Rinse tweezers with DI water. Dry with air.
11. Pour Hydrogen Peroxide into the “Piranha” beaker (Make sure that pour Hydrogen Peroxide into Sulfuric acid.)
12. Place staining rack in the Piranha solution. Full personal protective gear must be worn.

13. Start the timer for 20 minutes.
14. Rinse tweezers with DI water. Dry with air.
15. Transfer staining rack to “DI Rinse” beaker (full of 200ml of DI water). Be sure the glass slides are completely covered with DI water.
16. Let stand in the DI water for 5 minutes.
17. Meanwhile
    a. Rinse tweezers with DI water. Dry with air.
    b. Aspirate the waste Piranha solution followed by a large amount of DI water (Fill Piranha solution rinse beaker half with DI water. Pour half of Piranha solution in this beaker. Repeat the above steps and dissipate all Piranha solution.) (Make sure that pour Piranha solution into DI water.)
18. Rinse the “IPA” beaker with IPA. Fill with 100ml DI and 100 ml IPA.
19. Transfer staining rack to “IPA” beaker.
20. Aspirate the waste from the “DI Rinse” beaker.
21. Clean the tweezers with acetone/IPA/DI/IPA.
22. Rinse each glass slide with IPA.
23. Dry with air.

Appendix B

Materials Used for Glass Cleaning with Piranha Solution

Chemical materials:

1. IPA (Isopropyl alcohol) (~200 mL)
2. DI (Distilled water) (~3L)
3. Acetone
4. 96% Sulfuric Acid (160 mL)
5. 30% Hydrogen Peroxide (40mL)

Laboratory Apparatus:

1. Four 250 ml beaker
2. One 1000mL beaker
3. One 50mL measuring cylinder
4. One 100mL measuring cylinder
5. Full personal protective gear
6. Tweezers
7. Ceramic staining rack
8. Cleaning wipe
9. Sonicator
10. Timer

Appendix C

2404 Temperature Controller / Programmer

The high temperature furnaces was controlled by a 2404 temperature controller / programmer made by Schneider Electric. Figure 1 and 2 show the layout of the front panel for the model 2402 temperature controller / programmer.

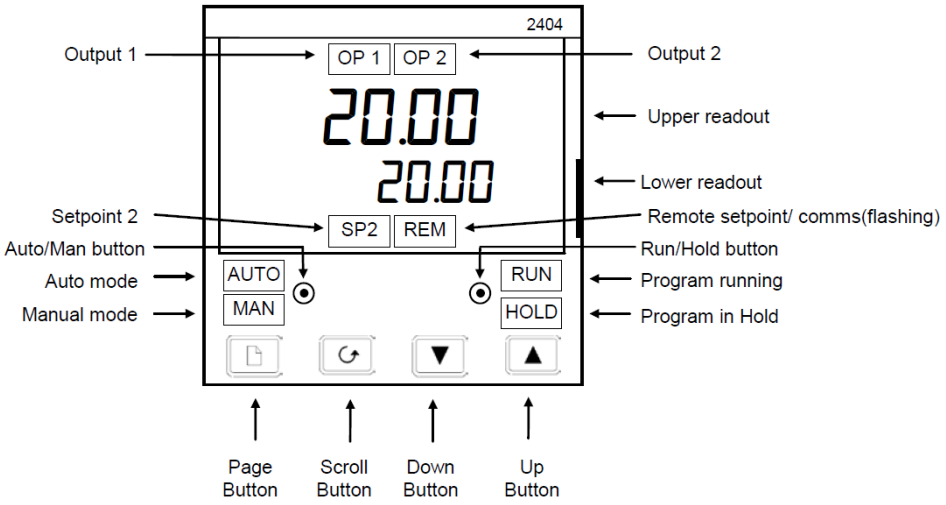


Figure 1. Model 2404 Front Panel Layout (Figure from the user manual)

Figure 2. Model 2404 Actual Front Panel Layout (Figure from the user manual)

Table 1 is a summary of the most common buttons and indicators used in the operation of the model 2404 controller / programmer from the user manual. For detailed operation procedures, please see chapter 5 of the user manual for reference.

Table 1. Controller Buttons and Indicators

Button or indicator	Name	Explanation
OP1	Output 1	When lit, it indicates that the output installed in module position 1 is on. This is normally the heating output on a temperature controller.
OP2	Output 2	When lit, it indicates that the output installed in module position 2 is on. This is normally the cooling output on a temperature controller.
SP2	Setpoint 2	When lit, this indicates that setpoint 2, (or a setpoint 3-16) has been selected.
REM	Remote setpoint	When lit, this indicates that a remote setpoint input has been selected. 'REM' will also flash when communications is active.
	Auto/Manual button	When pressed, this toggles between automatic and manual mode: • If the controller is in automatic mode the AUTO light will be lit. • If the controller is in manual mode, the MAN light will be lit. The Auto/Manual button can be disabled in configuration level.
	Run/Hold button	• Press once to start a program (RUN light on.) • Press again to hold a program (HOLD light on) • Press again to cancel hold and continue running (HOLD light off and RUN light ON) • Press and hold in for two seconds to reset a program (RUN and HOLD lights off) The RUN light will flash at the end of a program. The HOLD light will flash during holdback or when a PDS retransmission output is open circuit.
	Page button	Press to select a new list of parameters.
	Scroll button	Press to select a new parameter in a list.
	Down button	Press to decrease a value in the lower readout.
	Up button	Press to increase a value in lower readout.

For the programming operation, the very first thing is to understand five different types of segment and different program states which is showed in Table 2 and 3 from the user manual.

Table 2. Segment Types

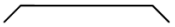
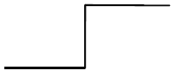
Ramp		**The setpoint ramps linearly**, from its current value to a new value, either at a set rate (called *ramp-rate programming*), or in a set time (called *time-to-target programming*). You must specify the ramp rate or the ramp time, and the target setpoint, when creating or modifying a program.
Dwell		**The setpoint remains constant** for a specified period.
Step		**The setpoint steps instantaneously** from its current value to a new value.
Call		**The main program calls another program as a subroutine**. The called program then drives the setpoint until it returns control to the main program. This facility is available on those controllers with 4, or 20, stored programs.
End		**The program either ends in this segment, or repeats.** You specify which is the case when you create, or modify, the program (see the final topic in this chapter). When the program ends, the programmer is put into either, a continuous Dwell state with all outputs staying unchanged, or the Reset state, or to a settable power level.

Table 3. Program States

State	Description	Indication
Reset	In Reset, the programmer is inactive and the controller behaves as a standard controller, with the setpoint determined by the value set in the lower readout.	**Both the RUN and HOLD lights are OFF**
Run	In Run, the programmer varies the setpoint according to the active program.	**RUN light on**
Hold	In Hold, the program is frozen at its current point. In this state you can make temporary changes to any program parameter (for example, a target setpoint, a dwell time, or the time remaining in the current segment). **Such changes will only remain effective until the program is reset and run again, when they will be overwritten by the stored program values.** ***Note:*** When a program is running, you cannot alter a **cALLed** program until it becomes active within that program.	**HOLD light on**
Holdback	Holdback indicates that the measured value is lagging the setpoint by more than a preset amount and that the program is in Hold, waiting for the process to catch up. See *Holdback* in the section on Automatic behaviour later this chapter.	**HOLD light flashes**
	A master controller can re-transmit a setpoint value to a number of slave units using PDSIO setpoint retransmission. Any of the slave units can generate a holdback signal which will also flash the **HOLD** light. Holdback will also occur if the PDSIO output is open circuit. This can be disabled in configuration by selecting the PdS output as SPnH - 'setpoint retransmission without holdback'	**HOLD light flashes**
End	The program is complete.	**RUN light flashes**

Here is an example of how to program the temperature controller (assume we had to change program 4 to Ramp up rate = Cool down rate = 1 °C/min, Set point temperature = 600 °C, and dwell time = 10 hrs.).

1. Reach the ProG List header from the home display and select program 4.
2. Set Ramp and Dwell units to min by pressing down and up button..
3. Set number of program cycles to 1.
4. Set segment number to 1.
5. Set target set point to 600 by pressing down and up button.
6. Set Ramp rate to 1 and duration time to 600 by pressing down and up button.
7. Set Cool down rate to 1 by pressing down and up button.
8. Return to ProG List header and start program 4.